

Ivoclar AG, Bendererstrasse 2, FL-9494 Schaan, Liechtenstein

Synthesis, characterization and polymerization of**waxy monomers**

C 084 18 j 21 B 4

Norbert Moszner*, Urs Karl Fischer, Thomas Völkel, Volker Rheinberger

(Received 24 June 1996)

p. d. 03-1997

SUMMARY:

Waxy monomers and crosslinkers, respectively, were synthesized from commercially available waxes by esterification with 2-hydroxyethyl methacrylate, glycerol dimethacrylate, or glycidyl methacrylate or by functionalization with 2-isocyanatoethyl methacrylate. The resulting opaque methacrylates with melting points between 45 and 80 °C were polymerized in bulk and in toluene solution in presence of free radical initiators. The obtained polymers were characterized by a broad molecular weight distribution. Opposite to the bulk polymerization, the double bond conversion in solution polymerization is nearly quantitative. The observed volume shrinkage during polymerization is very low due to the high molecular weight of the monomers. Polymerizates containing crosslinking comonomers exhibit improved mechanical stability.

ZUSAMMENFASSUNG:

Wachsartige Monomere und Vernetzer wurden aus kommerziellen Wachsen durch Veresterung mit 2-Hydroxyethylmethacrylat, Glycerindimethacrylat oder Glycidylmethacrylat oder durch Funktionalisierung mit 2-Isocyanatoethylmethacrylat synthetisiert. Die erhaltenen opaken Methacrylate mit Schmelzpunkten zwischen 45 und 80 °C wurden in Substanz bzw. Toluollösung in Gegenwart von Radikalinitiatoren polymerisiert. Die Polymeren zeichnen sich durch eine breite Molmassenverteilung aus. Im Gegensatz zur Substanzpolymerisation ist der Doppelbindungsumsatz nach der Lösungspolymerisation nahezu vollständig. Aufgrund der hohen Molmasse der Monomeren ist der beobachtete Polymerisationsschrumpf sehr gering. Polymerisate mit Vernetzermomeren zeigen eine verbesserte mechanische Stabilität.

Introduction

In general, waxes^{1,2} are considered as non-glassy solid materials which can be moulded at 20 °C. They show a melting point higher or equal than 40 °C. They are insoluble in water and in most cases lustrous when applied

* Correspondence author.

in thin layers. Besides, waxes can be polished under slight pressure. Consistency and solubility depend strongly on temperature. Natural occurring and synthetic derivatives of fatty acids and long chain hydrocarbons exhibit properties of waxes.

One important technical application of waxes are materials for casting and embedding. In dental techniques they are used as casting and modelling material for prosthesis fabrication. For these applications the products should easily be workable and should show sufficient dimensional stability at oral temperatures. Mixtures of paraffinic, stearic, Japanese, and bee waxes have been used³.

Normally, the waxes are melt before treatment. The melt is poured into the mould and the wax congeals in this form. Due to the temperature change, shrinkage of the wax occurs which causes fractures and cracks in the material. To overcome these problems, mixtures of waxes and polyfunctional monomers based on methacrylates, acrylates^{4,5}, and styrene derivatives⁶ are used. These mixtures can be hardened by photocuring to give better mechanical stability. In these polymerized waxes phase separation proceeds, leading to cracks and decreasing the long-term mechanical stability.

Our aim was to synthesize waxy compounds with improved properties and polymerizable groups, like methacrylates and acrylates. Recently, wax substitutes based on multifunctional monomers were described⁷.

The introduction of methacrylic and acrylic groups into waxy long chain alcohols has already been described⁸⁻¹¹. But these products have melting points lower than room temperature.

Experimental

Materials

Toluene, tetrahydrofuran (THF), and 2-hydroxyethyl methacrylate (HEMA) were dried over molecular sieve before use. Hoechst wax S (HS, acid number 140 mg KOH/g) and Hoechst wax KST (OH number 18 mg KOH/g) were purchased from Hoechst. 2-Isocyanatoethyl methacrylate (IEMA, Polyscience), glycidyl methacrylate (GMA, Röhm), glycerol dimethacrylate (GMDA, Röhm), Metatin 812 (Acima), and 1,2-octadecanediol (OD), ethyl chloroformate, 1,4-diazabicyclo[2.2.2]octane (DABCO) and collidine (Fluka) were used without further purification.

Syntheses

OD-IEMA (addition of 2 equivalents IEMA to OD):

7.8 g (50.3 mmol) IEMA is added to a solution of 7.4 g (25.6 mmol) OD and 20 mg Metatin 812 in 80 mL THF. The temperature must not rise above 26°C. After stirring for 5 d at room temperature, the solvent is removed and 14.6 g (yield 97%) of a white, waxy solid remains (m. p. 42°C).

(C ₃₂ H ₅₆ N ₂ O ₈) (596.8)	calc.	C 64.42	H 9.53	N 4.65
	found	C 64.38	H 9.41	N 4.61

¹H NMR (90 MHz, CDCl₃, ppm δ): 5.6 (s, 2H) and 6.1 (s, 2H), =CH₂; 5.2 (t, 2H), NH; 5.0 (m, 1H), >CHO; 4.2 (t, 6H), CH₂O; 3.5 (t, 4H), CH₂N; 1.9 (s, 6H), CH₃; 1.1–1.3 (br, 30H), CH₂; 0.9 (t, 3H), CH₃.

IR (film): 3365 (N—O), 2835 (C—H), 1720 (C=O), 1637 cm⁻¹ (C=C).

HS-HEMA (HS esterified with HEMA):

A mixture of 70 g HS (186.7 mmol) 22.6 g collidine (186.7 mmol) and 20.3 g ethyl chloroformate (186.7 mmol) in 1000 mL toluene is stirred for 72 h under anhydrous conditions. Then 24.4 g HEMA (186.7 mmol) and 0.1 g p-toluenesulfonic acid as catalyst are added and stirred for 3 d at 60°C. The mixture is filtered at 60°C. After 12 h at 4°C a white, voluminous solid precipitates from the filtrate. It is washed twice with ethanol and slightly acidified (HCl) water and dried in a desiccator over anhydrous CaCl₂. 60 g (yield 70%) of colourless, waxy solid remains (m.p. 47°C to 61°C, by DSC).

¹H NMR (90 MHz, CDCl₃, ppm δ): 5.6 (s, 1H) and 6.2 (s, 1H), =CH₂; 4.3 (t, 2H), CH₂O; 2.2 (t, 2H), CH₂COO; 1.9 (s, 1.4 H), CH₃; 1.2–1.4 (br, 50 H), CH₂; 0.9 (t, 3H), CH₃.

IR (film): 3400 (O—H), 2915 (C—H), 1731 (C=O), 1639 (C=C), 1157 cm⁻¹ (C—O).

HS-GMA (reaction of HS with GMA):

A mixture of 40 g (0.11 mol) HS, 44.6 g (0.31 mol) GMA and 0.7 g DABCO in 600 mL toluene is stirred at 65°C for 5 d. After volume reduction to 100 mL, the mixture is stored over night at 4°C. The resulting precipitate is filtered and washed twice with ethanol and slightly acidified water. After drying over anhydrous CaCl₂, 51 g (yield 100%) of a white, waxy solid remains (m. p. 40–67°C, by DSC).

¹H NMR (90 MHz, CDCl₃, ppm δ): 5.8 (s, 1H) and 6.3 (s, 1H), =CH₂; 4.3–4.7 (m, 4.5H), HOCH—CH₂; 2.4–2.6 (m, 2H), CH₂—C=O; 2.2 (s, 2H), CH₃; 1.1–1.7 (br, 50 H), CH₂; 0.9 (t, 3H), CH₃.

IR (film): 3368 (N—H), 2927 (C—H), 1719 (C=O), 1638 cm⁻¹ (C=C).

HS-GDMA (HS esterified with GDMA):

A mixture of 140 g HS (373.4 mmol), 45.2 g collidine (373.4 mmol) and 40.5 g ethyl chloroformate (373.4 mmol) in 1 000 mL toluene is stirred for 72 h under anhydrous conditions. Then 85.2 g GDMA (373.4 mmol) and 0.1 g p-toluenesulfonic acid is added and stirred for 3 d at 60°C. The mixture is filtered at 60°C. After 2 d at 4°C a white, voluminous solid precipitates from the filtrate. It was washed twice with ethanol and slightly acidified water and dried in a desiccator over anhydrous CaCl_2 . 80 g (yield 50%) of a colourless, waxy solid remains (m.p. 55°C to 77°C, by DSC).

^1H NMR (90 MHz, CDCl_3 , ppm δ): 5.6 (s, 1 H) and 6.2 (s, 1 H), $=\text{CH}_2$; 4.0–4.5 (m, 3 H), CH_2O and CHO ; 2.2 (t, 2 H), CH_2COO ; 1.9 (s, 35 H), CH_3 ; 0.8–1.6 (br, 35 H), CH_2 and CH_3 .

IR (film): 3450 (O—H), 2918 (C—H), 1737 (C=O), 1638 (C=C), 1171 cm^{-1} (C—O).

KST-IEMA (adduct of KST with IEMA):

A solution of 15 g (10 mmol) KST, 2.1 g (20 mmol) IEMA, and 2 drops of Metatrin 812 in 225 mL toluene is stirred at 60°C for 3 d. The solution is reduced to 80 mL and stored over night at 4°C. The resulting precipitate is washed twice with ethanol and slightly acidified water. After drying (desiccator over anhydrous CaCl_2) 6.7 g (yield 45%) of a waxy solid remains (m.p. 45°C).

^1H NMR (90 MHz, CDCl_3 , ppm δ): 5.7 (s, 1 H) and 5.0 (s, 1 H) $=\text{CH}_2$; 5.0 (br, 1 H), NH; 4.3 (t, 2 H), $\text{CH}_2\text{—O}$; 3.6 (br, 60), $\text{CH}_2\text{-wax}$; 3.5 (m, 2 H), CH_2N ; 2.0 (s, 3 H), CH_3 .

IR (KBr): 2918, 2849 (C—H), 1737 (C=O), 1637 cm^{-1} (C=C).

Polymerization

For the solution polymerization, the waxy monomer is dissolved in 40 mL toluene in a Schlenk tube. After three freeze-thaw cycles, 5 wt.-% of AIBN is added under argon. The solution is stirred at 80°C for 8 h or until gelation occurs, respectively. The soluble part is slowly dropped into 350 mL methanol. The formed precipitate is filtered off and dried at 0.1 hPa at room temperature. In case of the photopolymerization, the monomers, camphorquinone (CC) and N-(2-cyanoethyl)-N-methylaniline (CEMA) were mixed in a three-roll mill. The resulting waxes were melt and poured into heated moulds and cooled to room temperature. These moulds were irradiated in a commercial dental light curing device (SPECTRAMAT, Ivoclar) for different times.

Measurements

^1H NMR measurements were recorded on an EM 390 (Varian, 90 MHz) using tetramethylsilane (TMS) as internal standard. A FT-IR spectrometer 1600 (Perkin Elmer) was used to record IR spectra. The molecular weight and molecular weight distribution were determined by gel permeation chromatography (GPC) using an isocratic pump IsoChrom (Spectra-Physics), a RI detector (Varian) and columns (PSS) calibrated with poly(methyl methacrylate) standards. DSC measurements were performed using a DSC 7 (Perkin Elmer) with a heating rate of 10 K/min. The monomer samples were mixed with 2 wt.-% dibenzoyl peroxide and stored in a refrigerator before measurements.

Results and discussion

The functional waxes were modified to yield curable monomers (Tab. 1). The introduction of methacrylic groups in hydroxy compounds such as OD and Hoechst wax KST (KST, wax based on poly(ethylene oxide)) were carried out by addition of IEMA (Scheme 1).

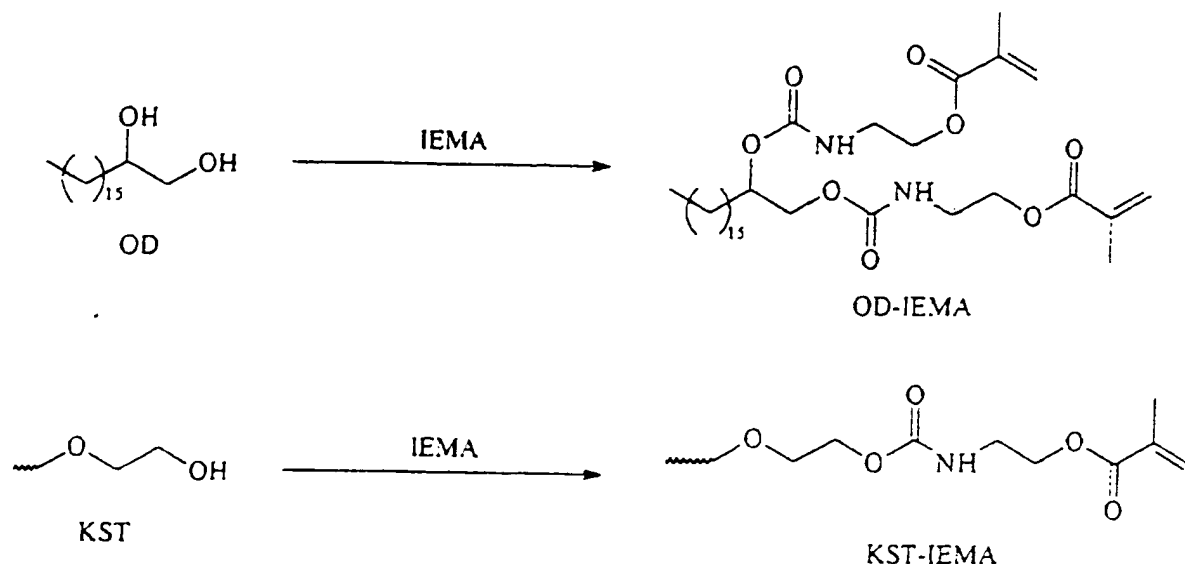
Tab. 1. Melting points of the educts and products of modification.

Educt	m. p. (°C)	Modified by	Product	m. p. (°C)
1,2-Octadecanediol	74–76	IEMA	OD-IEMA	42
Hoechst wax S	80	HEMA	HS-HEMA	47–61
Hoechst wax KST	57–59	IEMA	KST-IEMA	45
Hoechst wax S	80	GMA	HS-GMA	40–67
Hoechst wax S	80	GDMA	HS-GDMA	55–77

Hoechst wax S (HS) is a mixture of aliphatic C_{16} – C_{36} carboxylates. The carboxylic groups were activated according to the mixed anhydride method¹² by reaction with ethyl chloroformate. In a second step, the esterification with HEMA and GDMA, respectively, was carried out (Scheme 2). Finally, a polymerizable product was obtained by treating Hoechst wax S with GMA according to¹³.

The products were characterized by IR and ^1H NMR spectroscopy. The conversion of the modification of the starting waxy compounds was calculated based on the integral ratio of the introduced methacrylic double bonds and the chain CH_2 -groups (Tab. 2). Introduction of methacrylates by isocyanates succeeded quantitatively. The ring opening reaction of GMA showed

Scheme 1:



Tab. 2. Content of methacrylic groups introduced into the waxy monomers and conversion of the double bonds during bulk polymerization measured by DSC.

Product	Content of methacrylic groups ^a (mol-%)	Conversion of double bonds ^b (%)
OD-IEMA	100	100
HS-HEMA	48	100
HS-GMA	90	69
KST-IEMA	100	42
HS-GDMA	64	78

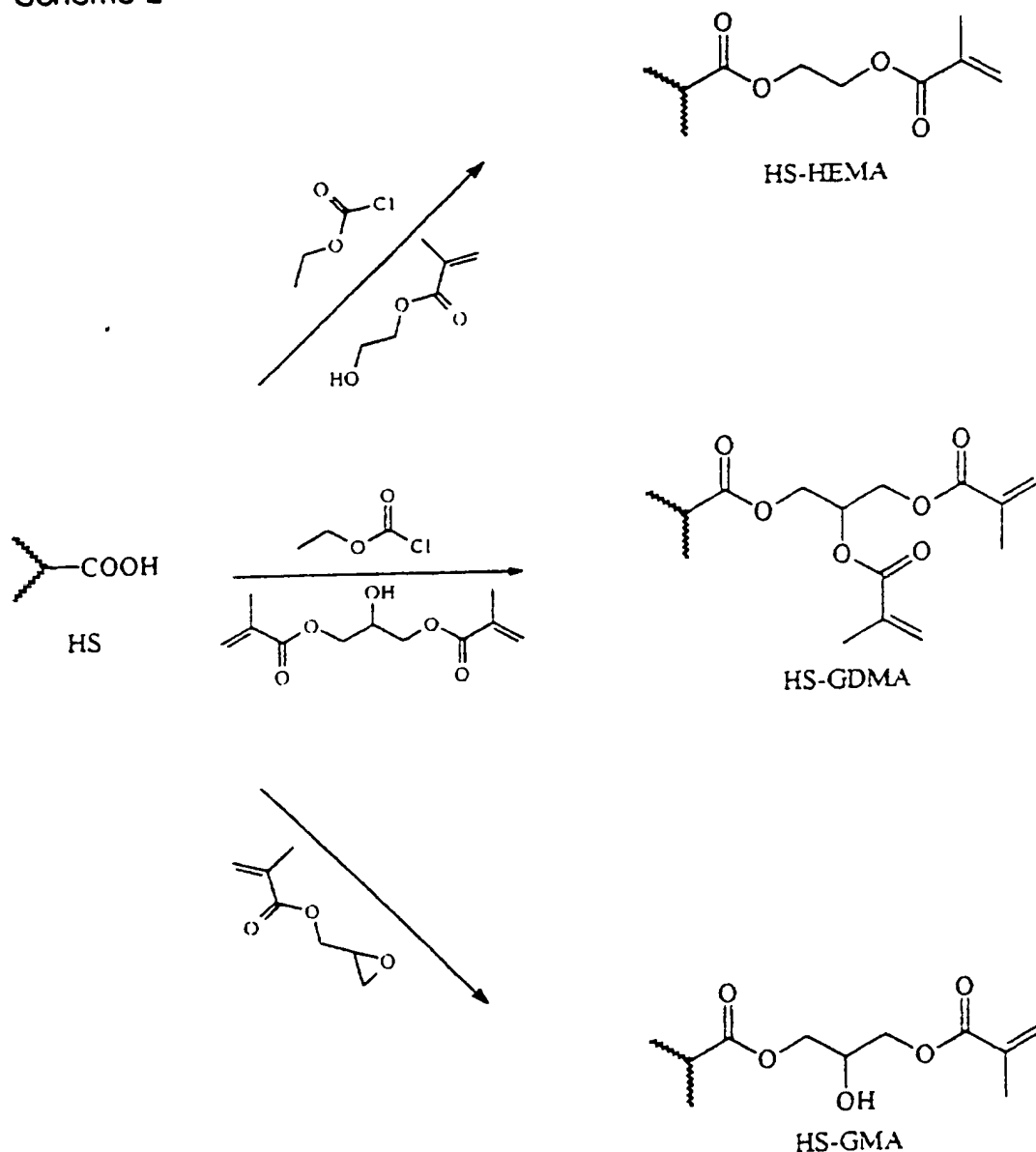
^a Estimated by ¹H NMR.

^b Calculated from ΔH_p compared with ΔH_p from lauryl methacrylate as standard.

also sufficient results. On the other hand, only 48–62% conversion was realized in the two step esterification with HEMA and GDMA, respectively.

The melting points of the polymerizable products were generally lower than the melting points of the corresponding educts, even after reaction with IEMA, where urethane groups were formed. By DSC, bulk polymerization was carried out with a constant heating rate of 10 K/min. Because of the low melting points the polymerization reaction took place in the molten state. The determined polymerization enthalpy could be compared with the theoretical enthalpy value calculated from lauryl methacrylate. By this way it could be shown that the double bond conversion is quantitative for OD-IEMA and HS-HEMA.

Scheme 2:



Furthermore, the polymerization was also carried out in toluene solution with AIBN at 80°C. The studied compounds were well soluble in toluene at elevated temperature. In solutions of 0.1 mol/L and in case of di- and higher functional monomers, respectively, gelation occurred (Tab. 3).

The soluble part of polymers showed a broad molecular weight distribution probably due to the formation of branches. HS and KST were already polydisperse before modification. The conversion of the double bonds was nearly quantitative though the polymerization was carried out in highly diluted solutions.

Homopolymers of OD-IEMA and HS-HEMA, respectively, were obtained by irradiation in the solid state with camphorquinone (CC) and 2-cyanoethyl methyl aniline (CEMA) as initiator for 20 min (Tab. 4).

Tab. 3. Results of the polymerization of waxy monomers in toluene (8 h at 80°C with 5 wt.-% AIBN).

Monomer	Concentration (mmol/L)	Conversion of the double bonds (%)	Gelation time (min)	Gel content (%)	M_n^a	M_w/M_n
OD-IEMA	20	95 ^b	—	0	5 240	(3.3)
HS-HEMA	20	100 ^b	—	0	11 920	(5.2)
KST-IEMA	20	about 100 ^c	150	100	—	—
HS-GDMA	20	100 ^b	— ^d	18	6 890	(4.0)
HS-GMA	20	100 ^b	—	0	5 780	(3.8)
HS-GDMA	100	100 ^{b,c}	240	43	—	—

^a From GPC, calculated with poly(methyl methacrylate) standards.

^b Calculated from ¹H NMR of the soluble part of the polymer.

^c Determined by IR.

^d Because of the swelling in toluene no gelation could be detected.

Tab. 4. Shrinkage of the homopolymers^a.

Monomer	Shrinkage (%)
OD-IEMA	1.2
HS-HEMA	0.8
HS-GMA	0.7
HS-GDMA	0.8
KST-IEMA	2.2

^a The monomers were irradiated in solid state for 20 min.

According to the high molecular weight of these monomers, the volume shrinkage was significantly lower in comparison to other methacrylates.

The waxy monomer HS-HEMA was copolymerized with different acrylates like OD-IEMA, pentaerythritol tetraacrylate (PETA) or ethoxylated bisphenol A diacrylate (EBDA). The waxy state of these mixtures did not change. The consistency of the resulting monomer mixtures was the same as of dental waxes.

The resulting irradiated polymerizates were waxy and opaque and showed improved mechanical strength (Tab. 5). Further improvement of mechanical properties of the waxes could be realized by filling e. g. with pyrogenic silica (OX-50). The filled, uncured wax melt but it did not flow like unfilled

Tab. 5. Compositions and properties of polymerizates containing HS-HEMA, initiator 0.3 wt.-% CC/0.6 wt.-% CEMA.

Comonomer	Comonomer content (wt.-%)	Compressive strength (MPa)	Flexural strength (MPa)	Elasticity modulus (MPa)
OD-IEMA ^a	61.4	23	—	—
PETA ^a	37.3	—	5	1010
EBDA ^b	36.9	—	11	990
PETA ^{b,c}	31.3	—	31	2800

^a Irradiation time 6 min.

^b Irradiation time 20 min.

^c Filler content 29.9 wt.-% OX-50 (Degussa).

waxes. Mechanical properties were not improved after irradiation at higher temperatures.

These filled and unfilled waxes could be used for dental applications. Ordinary waxy models of crowns are weak and fragile but irradiated crowns based on materials as described above showed a significantly improved stability. For example, after storage of an unirradiated crown model for 30 min at 60°C no dimensional change was observed. During cooling of the uncured wax model, cracks due to thermal shrinkage occurred. In contrast to this, the polymerized wax models showed no cracks under the same conditions.

We would like to thank Dr. Wildgruber (Hoechst AG) for supplying the Hoechst waxes.

¹ J. J. Kaufman, A. W. Stratton, *Encycl. Polym. Sci. Eng.*, Vol. 17 (1989), p. 784

² G. Illmann, H. Schmidt, W. Brotz, G. Michalczyk, W. Payer, C. D. Frohning, W. Dietsche, G. Hohner, J. Wildgruber, *Ullmanns Encycl. Tech. Chem.*, Vol. 22 (1982), p. 1

³ K. Körber, K. Ludwig, "Zahnärztliche Wirkstoffe und Technologie", G. Thieme, Stuttgart 1982, p. 89

⁴ Jpn. 92/4748 (1992), *Nippon Catalytic Chem. Ind., Invs.*: M. Kushino, R. Kitada, Y. Mori, T. Yoneda, *Chem. Abstr.* **120** (1993) 136156

⁵ Jpn. 90/312256 (1990), *Toeï Sangyo K. K., Inv.*: S. Ieda, *Chem. Abstr.* **118** (1992) 27523

- ⁶ Jpn. 91/330047 (1991), Mitsubishi Paper Mills Ltd., Invs.: K. Yabuta, H. Sekiguchi, Chem. Abstr. **119** (1993) 282306
- ⁷ Eur. Pat. 443 269 (1990), Invs.: J. D. Oxman, L. S. Kangas, F. A. Ubel, Chem. Abstr. **116** (1992) 67263
- ⁸ C. E. Rehberg, C. H. Fisher, J. Am. Chem. Soc. **66** (1944) 1203
- ⁹ C. E. Rehberg, W. A. Faucette, C. H. Fisher, J. Am. Chem. Soc. **66** (1944) 1723
- ¹⁰ B. Subrahmanyam, S. D. Baruch, M. Rahman, N. C. Laskar, R. K. Mazumder, Polymer **35** (1994) 862
- ¹¹ S. D. Baruch, N. C. Laskar, B. Subrahmanyam, J. Appl. Polym. Sci. **51** (1994) 1701
- ¹² G. Friedmann, H. Aichaoui, M. Brini, Makromol. Chem. **182** (1981) 337
- ¹³ Ger. Pat. 2359491 (1974), Inv.: H. Jandourek, Chem. Abstr. **81** (1974) 171512v